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(54) METHOD AND EQUIPMENT FOR CLEANING SILICON

(57)Abstract:
PROBLEM TO BE SOLVED: To prevent generation of a water mark in drying by subjecting a substrate having silicon surface to wet cleaning, rinsing the silicon surface with pure water and then forming an oxide film of specified thickness on the silicon surface during or after rinsing before drying.
SOLUTION: A substrate having silicon surface is subjected to wet cleaning and the silicon surface is rinsed with pure water. An oxide film of 10-30 Åis then formed on the silicon surface during or after rinsing before the silicon surface is dried. Alternatively, a substrate having a native oxide film on the surface is subjected to wet etching in order to remove the native oxide and the silicon surface is rinsed with pure water. An oxide film of 10-30 Å is then formed on the silicon surface during or after rinsing before the silicon surface is dried. The oxide is preferably formed using pure water added with an oxidizing agent.

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CLAIMS

[Claim(s)]

[Claim 1] The washing approach of the silicon which carries out the rinse of the silicon front face with pure water after washing wet for the substrate which has a silicon front face, and is characterized by drying a silicon front face after forming in a silicon front face in the rinse concerned and after a rinse before drying a 10-30A oxide film.

[Claim 2] The washing approach of the silicon which carries out the rinse of the silicon front face with pure water after removing the natural oxidation film concerned for the substrate which has silicon with which the natural oxidation film exists in a front face by wet etching, and is characterized by drying a silicon front face after forming in a silicon front face in the rinse concerned and after a rinse before drying a 10-30A oxide film.

[Claim 3] It is the washing approach of the substrate in front of the process which irradiates amorphous silicon and uses laser as polycrystalline silicon at it. After removing the natural oxidation film concerned by wet etching, the substrate which has amorphous silicon with which the natural oxidation film exists in a front face The washing approach of the silicon characterized by drying an amorphous silicon front face after carrying out the rinse of the amorphous silicon front face with pure water, and forming in an amorphous silicon front face in the rinse concerned and after a rinse before drying a 10-30A oxide film.

[Claim 4] The washing approach of the silicon according to claim 1 to 3 characterized by performing formation of said 10-30A oxide film to pure water with wet using the pure water which added the oxidizer.

[Claim 5] The pure water which added said oxidizer is the washing approach of the silicon according to claim 4 characterized by adding the hydrogen peroxide of 5 - 20 volume % to the thing or pure water which added the thing which added the ozone which electrolyzes and obtains pure water to pure water, or the ozone which irradiates ultraviolet rays and acquires them into oxygen to pure water.

[Claim 6] A means to be washing or the etching system of wet silicon, and to wash or etch silicon, The means which carries out the pure-water rinse of the silicon front face, and a means to supply the pure water which added the oxidizer to a silicon front face, The silicon washing station characterized by supplying the pure water concerned from a means to be equipment which has at least a means to carry out spin desiccation of the silicon front face, and to supply the pure water which added the pure water which added said oxidizer before drying a silicon front face with said means which carries out spin desiccation.

[Claim 7] The pure water which added said oxidizer is the washing station of the silicon according to claim 6 characterized by adding the hydrogen peroxide of 5 - 20 volume % to the thing or pure water which added the thing which added the ozone which electrolyzes and obtains pure water to pure water, or the ozone which irradiates ultraviolet rays and acquires them into oxygen to pure water.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the washing approach of silicon and washing station which the ********** water mark which remains decreases in the process which dries silicon after washing wet [on the front face of silicon], or etching in the field using silicon also in a semi-conductor.
[0002]
[Description of the Prior Art] Although divided into single crystal silicon, polycrystalline silicon, and amorphous silicon in the gestalt also in an ingredient called silicon, the semiconductor industry using silicon has a property as a semi-conductor in every gestalt, and since a raw material is on the earth at abundance, it is used in the large field. The polycrystalline silicon as computing elements, such as memory and CPUs, such as DRAM and EPROM, and MPU, is used as the switching transistor and drive circuit of a liquid crystal display, or a solar battery, and amorphous silicon is used for single crystal silicon as the switching transistor and solar battery of a liquid crystal display.
[0003] It is especially used for the integrated circuit which uses the function as a transistor also in application of each silicon in many cases. When using silicon for an integrated circuit, it is competing fiercely on clarification environmental structure, micro-processing equipment, and an ingredient technique to the sensitivity and ultra-fine processing technology of an impurity of the silicon especially.
[0004] When using silicon as a semi-conductor, the technique of washing and etching is indispensable. As for most washing, the wet approach is used. There are scrub washing which grinds and washes a front face with a brush etc. as washing for removing a physical-adsorption object, ultrasonic cleaning which is made to produce wave of expansion and is washed with the impact in pure water or a drug solution with a supersonic wave, megasonic washing, etc. As washing for removing the organic substance adhering to a front face, silicon is put into the inside which mixed the sulfuric acid to hydrogen peroxide solution, and there is washing which removes the organic substance by the chemical reaction. washing which puts silicon into the inside which mixed the hydrochloric acid to hydrogen peroxide solution as washing which removes metal contamination, and removes a metal contamination by the chemical reaction -- such -- **.
[0005] There is wet etching using the dry etching and the drug solution which used gas among the etching. Wet etching using a drug solution is used also in etching of the large whole front face, and micro processing of a semi-conductor to what has a comparatively large processing dimension.
[0006] Thus, in semiconductor technology, the present condition is that many wet processes are used for washing, etching, etc. In the process wet [this], the water mark poses a big problem. When drying the substrate which has a silicon front face after wet washing or etching, while being from the condition in which the substrate was damp to a water mark in dryness, waterdrop adheres to a substrate front face and adhering waterdrop is lost by desiccation, but after waterdrop is lost, it is the phenomenon in which the marks of the waterdrop remain.
[0007] There is still no suitable Japanese of a water mark among these contractors. Various expressions, such as silverfish of ****, the remains of waterdrop, and water, are used, and it calls as a water mark in this specification. There is no technical interpretation with what still steadfast a water mark is, and it has not come out of the hypothetical region.

[0008] There are three elements which cannot be lacked as a phenomenon which can do a water mark. ** Silicon ** oxygen ** water It is three. A water mark will not be generated if at least one of these three is missing. What is depended on accepted theory (for example, monthly publication Semiconductor World 1996.3p92-94) is shown in drawing 3 . The oxygen in a desiccation ambient atmosphere does a dissolution of at the waterdrop (H2 O) pure water which adhered on the surface of silicon. b diffusion of the oxygen which dissolved is done at the silicon front face and the interface of waterdrop. c oxide is formed on a silicon front face. d elution of is done and the formed oxide is a silicic acid (considered H2SiO3). It becomes. A silicic acid is further diffused, after carrying out e diffusion and dissociating in liquid. After waterdrop dries, a silicon oxide remains in a silicon front face, and this is considered to be a water mark.

[0009] Once a water mark is formed, it is substantially [that it is very difficult and] unremovable to remove it. Therefore, silicon remains, without the ability not etching in a part to act as a mask and etch at the time of etching of next silicon, because of a water mark, or etching partially.

[0010] The numerousness of water marks and the number on a substrate change with the conditions when being formed a lot. With 1 micrometer phi-60 micrometerphi extent, magnitude has a number, even when exceeding -1000 piece partly on the substrate of 5inchphi or a 5 inch angle. Occasionally, the thing of hundreds of micrometerphi may be formed partly.

[0011] Once it generates, since removal is difficult, as for a water mark, it is important how generating is prevented. As a policy which prevents generating of a water mark, it is together put by two points.

** Make it not arrange silicon, oxygen, and three conditions of water.

** Don't give the time amount which reacts (time amount from rinsing to desiccation is shortened as much as possible).

** Although there is the spin drying method for meaning making it dry in an instant, rotating a substrate in fact, and drying a substrate using an air current and a centrifugal force if it corresponds, this approach cannot be dried for a short time, so that it does not make a water mark form. Therefore, the spin drying method is unsuitable to desiccation on the conditions to which ** is equal.

[0012] There is an IPA (called isopropyl alcohol or propyl alcohol, and propanol) steam seasoning method as an approach of realizing losing short-time desiccation and water. This heats IPA and generates a steam. If a substrate is put in into the IPA steam filled in the tub in a dryer, the steam of IPA will dew on a substrate and will be permuted in the moisture and short time on a substrate. Since according to this IPA steam seasoning approach water is lost among three conditions of ** in order that water and IPA may permute for a short time, and desiccation of the short time of ** can carry out to coincidence, generating of a water mark can be prevented at a remarkable rate. Therefore, in almost all the cases of the process using the present silicon semi-conductor, it is applied.

[0013] As an approach of the latest [other], desiccation systems, such as a MARANGONI method and an IPA direct permutation method, are also proposed, and, partly, it is actually beginning to be used.

MARANGONI -- law pulls up a substrate in the ambient atmosphere of IPA+ nitrogen out of pure water slowly, and uses the surface tension of the pure water at that time, it is the same as an IPA direct permutation method, and a water mark is theoretically made as for it to zero.

[0014] Moreover, although the method dried in nitrogen-gas-atmosphere mind, the reduced-pressure-drying method dried in the state of reduced pressure are proposed within the closing system as a method which loses oxygen among three conditions which a water mark generates In the case of the carry Ares method (or sheet method) which processes only a substrate also by the carrier method processed where a substrate is put into the usual carrier without putting a substrate into a carrier It is difficult to lose oxygen completely also in the space made closing, and oxygen cannot be permuted by other gas, such as nitrogen, in a short time, either. Water and oxygen exist and this method is also very difficult for it until it also makes a reduced-pressure-drying method reduced pressure.

[0015] The approach of the conventional water mark generating prevention mentioned above was a thing to losing the silicon of three equal conditions of water mark generating, oxygen, the oxygen of the water, or water, or a thing which performs desiccation as much as possible for a short time. There is also a method of losing silicon among three equal conditions. A water mark will not be generated if the natural oxidation film exists in a silicon front face (above-mentioned Semiconductor World 1996.3p92-94). However, it is

important how the natural oxidation film is thinly controlled by this approach, and component degradation is caused by the thick natural oxidation film which is not controlled. Moreover, it cannot use at the process which is not allowed existence of few natural oxidation film, either.

[0016] As the production approach of a thin oxide film, the chemical oxide-film production approach indicated by "ultra clean ULSI technique, Tadahiro Omi work, and Baifukan" p214 is learned. This chemical oxide film production approach is applied before the process which forms the important gate oxide at the time of producing an insulated gate field effect transistor on silicon in a silicon front face especially. Formation of gate dielectric film forms oxidation silicon in a silicon front face using the oxidizing [thermally] method by the dry oxidation technique. Since the channel for pouring a carrier to the interface of the oxidization silicon and silicon is formed, after washing a silicon front face, it is formed in order to prevent polluting a silicon front face, while conveying even an oxidation system.

[0017] The silicon with which the chemical oxide film was formed is moved to a thermal oxidation process as it is, and the thermal oxidation film is formed on a chemical oxide film. A chemical oxide film turns into a part of gate oxide as it is. Therefore, the process which forms a chemical oxide film becomes complicated.

[0018] The production procedure for forming a chemical oxide film is shown in Table 1. A chemical oxide film is formed [a wet process]·for five processes and a dry type process through a total of six processes of one process.

[0019]

[Table 1]

処理液	組成	使用温度	処理時間
SPM	$H_2SO_4:H_2O_2=4:1$	120 ℃	5 分
O_3/H_2O	超純水+O_3 (2ppm)	室温	20 分
hot H_2O_2	30% H_2O_2	80-90 ℃	10 分
APM	$NH_4OH:H_2O_2:H_2O=0.05:1:5$	80-90 ℃	10 分
HPM	$HCl:H_2O_2:H_2O=1:1:6$	80-90 ℃	10 分
低温酸化	ドライO_2	800 ℃	20 分

[0020] Forming this chemical oxide film on the silicon after a washing process can prevent generating of a water mark. Since it is the oxide film controlled by the precision, unlike the natural oxidation film, thickness control is also carried out, and there are also few impurities. However, as for introducing the process which boils all at the washing process of usual silicon, and forms this chemical oxide film, a routing counter will increase sharply.

[0021] this invention person paid his attention to silicon among three conditions that it must not arrange for preventing generating of a water mark. The method of using a chemical oxide film considered forming the oxide film controlled by the simpler means from the process being complicated. Although washing or etching is carried out for a substrate, a pure-water rinse is performed and desiccation is performed after that, it is among the rinse or after a rinse, and results in a header and this invention that the thin oxide film controlled before desiccation can be formed in a silicon front face.

[0022]

[Problem(s) to be Solved by the Invention] That is, since this invention prevents generating of a water mark, in the approach of not arranging silicon among three conditions (silicon, oxygen, water) of water mark generating, not using a complicated process like a chemical oxide film, the natural oxidation film which is not control is not use, a subsequent process and a subsequent component property will be consider and the

natural oxidation film will be remove rather again. The oxide film controlled by the simple approach in pure water in the pure-water rinse after washing or etching and after the rinse by the front face of the silicon with which the natural oxidation film does not exist is produced, and it aims at offering the washing approach of preventing generating of a water mark at the time of desiccation.

[0023]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, invention indicated on these specifications is the washing approach of the silicon which carries out the rinse of the silicon front face with pure water after washing wet for the substrate which has a silicon front face, and is characterized by drying a silicon front face after forming in a silicon front face in the rinse concerned and after a rinse before drying a 10-30A oxide film.

[0024] Other invention indicated on these specifications is the washing approaches of the silicon which carries out the rinse of the silicon front face with pure water after removing the natural oxidation film concerned for the substrate which has silicon with which the natural oxidation film exists in a front face by wet etching, and is characterized by to dry a silicon front face after forming in a silicon front face in the rinse concerned and after a rinse before drying a 10-30A oxide film.

[0025] Other invention indicated on these specifications is the washing approaches of the substrate in front of the process which irradiates amorphous silicon and uses laser as polycrystalline silicon at it. After removing the natural oxidation film concerned by wet etching, the substrate which has amorphous silicon with which the natural oxidation film exists in a front face After carrying out the rinse of the amorphous silicon front face with pure water, and forming in an amorphous silicon front face in the rinse concerned and after a rinse before drying a 10-30A oxide film, it is the washing approach of the silicon characterized by drying an amorphous silicon front face.

[0026] In the washing approach of the above-mentioned silicon, it is desirable to perform formation of said 10-30A oxide film with wet using the pure water which added the oxidizer to pure water. Moreover, as for the pure water which added said oxidizer, it is desirable to add the hydrogen peroxide of 5 - 20 volume % to the thing or pure water which added the thing which added the ozone which electrolyzes and obtains pure water to pure water, or the ozone which irradiates ultraviolet rays and acquires them into oxygen to pure water.

[0027] A means for other invention indicated on these specifications to be washing or the etching systems of wet silicon, and to wash or etch silicon, The means which carries out the pure-water rinse of the silicon front face, and a means to supply the pure water which added the oxidizer to a silicon front face, It is equipment which has at least a means to carry out spin desiccation of the silicon front face. Before drying a silicon front face with said means which carries out spin desiccation, it is the silicon washing station characterized by supplying the pure water concerned from a means to supply the pure water which added the pure water which added said oxidizer.

[0028] Moreover, as for the pure water which added said oxidizer in the above-mentioned silicon washing station, what added the hydrogen peroxide of 5 - 20 volume % to the thing which added the ozone which electrolyzes and obtains pure water to pure water, the thing which added the ozone which irradiates ultraviolet rays and acquires them into oxygen to pure water, or pure water is desirable.

[0029] In the approach of not arranging silicon among three conditions (silicon, oxygen, water) of water mark generating in order that this invention may prevent generating of a water mark On the front face of the silicon with which the natural oxidation film does not exist, in the pure-water rinse after washing or etching, and after a rinse The washing station which is characterized by producing the oxide film controlled by the simple approach in pure water, and offers the washing approach of preventing generating of a water mark at the time of desiccation, and realizes this washing approach is offered.

[0030] After performing washing of wet silicon, or wet etching, the rinse by pure water is performed for the purpose which flushes a penetrant remover or etchant from a silicon front face. As for the inside of this rinse, pure water exists in the whole silicon, and since pure water is moreover flowing, a water mark does not occur. That is, while silicon exists in pure water after finishing the purpose of washing or etching, generating of a water mark can be prevented by forming the controlled oxide film.

[0031] The oxide film controlled by means to put in an oxidizer into pure water, in the pure water made into

the purpose of this invention is formed. Although there is washing for removing washing for washing for removal of a physical-adsorption object and removal of an organic substance affix and metal contamination etc. according to the purpose in case silicon is washed, the drug solution for washing is used in every washing. Moreover, at the wet etching process of silicon, etchant is used as a drug solution. In order to flush the drug solution and etchant for these washing from a silicon front face, the rinse by pure water is carried out.

[0032] The process of the rinse by pure water puts a substrate into a carrier, the whole carrier, it is **** wet washing or an etching process, and single wafer processing held only with a substrate, and, also as for the method of the rinse, the amount of pure water also differs also from time amount. However, in order to flush the drug solution which remains on a substrate front face to a certain fixed time amount, there is a process which pours pure water. At this rinse process, after the drug solution on the front face of a substrate is fully flushed, an oxidizer is added to the pure water for rinses, and an oxide film is formed in a silicon front face. Or it switches to the pure water with which the oxidizer was added from the pure water for rinses.

[0033] By this invention, instead of the pure water fundamentally used at the time of a pure-water rinse, if the rinse of the substrate is carried out for the pure water with which the oxidizer was added, an oxide film will be formed by passing similarly. There was no thought of making it dry, after forming an oxide film in the silicon front face made into clarification at a washing process before this invention.

[0034] As an oxidizer, as a result of the experiment of trial-and-error of many things [this invention people], when what added ozone to pure water, and the thing which added the hydrogen peroxide to pure water were used, it resulted in the conclusion that it is effective. In the case of the ozone which electrolyzes and obtains pure water as the generating approach of ozone, the method of irradiating ultraviolet rays at the oxygen in front of bubbling by the system to which bubbling of the oxygen is carried out for the inside of pure water, and generating ozone, and the rinse of single wafer processing, it turned out that the approach of irradiating ultraviolet rays is tried and all have effectiveness in a pure-water rinse.

[0035]

[Embodiment of the Invention] Although the silicon washing approach of this invention is applied in case it performs washing of silicon, or etching of silicon with wet, it processes a silicon front face with the drug solution for washing or etching a silicon front face first. Pure water is poured in order to flush the drug solution on the front face of silicon after that, after the processing purpose is attained (after what to wash was removable, or after what to etch was etched). If it is sheet processing, a sink and a pure-water rinse will be performed in pure water so that direct pure water may be sprayed on a silicon front face.

[0036] If it is a carrier method, what tub will also be used in the shape of a cascade, and a pure-water rinse will be performed so that a carrier may be attached to the tub containing the whole carrier with which the substrate which has a silicon front face was carried and pure water may be made to slush and overflow in the tub.

[0037] With a pure-water rinse, a drug solution fully produces a thin oxide film on a silicon front face, after being flushed. With a pure-water rinse, in the condition that pure water fully remains in the silicon front face, if an oxide film is not produced, it will become the cause which a water mark generates. If it is sheet processing, from a nozzle for the pure water which added the oxidizer beside the nozzle for spraying the pure water for rinses on a silicon front face to blow off, the pure water which added the oxidizer on the silicon front face will be sprayed on a silicon front face, the pure water for rinses will be stopped after that, and an oxide-film formation process will be performed.

[0038] Or the number of nozzles is one and they switch the pure water connected to the nozzle. A change is using an electro-magnetic valve or an air differential bulb, and switching to those of pure water and the pure water with which the oxidizing agent's was added with two line, and its change in an instant at a source side, and before waterdrop occurs on a silicon front face, it performs an oxidation process.

[0039] A substrate is copied the whole carrier to the tub which filled with the carrier method the pure water which added the oxidizer other than the tub which performs a pure-water rinse, and an oxidation process is performed. As the pure water which added the oxidizer in this tub flows as much as possible, it supplies the pure water of always new oxidizer addition.

[0040] The pure water of ozone addition is produced for the ozone which electrolyzed pure water into pure

water and it was made to generate as an approach of adding an oxidizer using the gas permeable membrane made of a fluororesin. The pure water which carried out ozone addition needs to enable it to produce the pure water of always new ozone addition by side of a washing station, since it is no longer aging when time amount is formed for ozone, even if added by pure water, in order to use it, before going through time amount as much as possible.

[0041] Moreover, some which added 5 - 20 volume % for the hydrogen peroxide have effectiveness in pure water as pure water which added the oxidizer. Although an oxide film will be formed if below 5% volume performs a rinse oxidation process over many hours, it takes process time amount too much. Moreover, if 20 volume % is exceeded, an oxidation rate will become large too much and control of the thickness of an oxide film will become difficult. Extent which is not applied so much by time amount, either and an oxidation rate does not have early so much, either is the addition which is about 5 - 20%.

[0042] In the phase which the washout of the drug solution by the rinse of a pure-water rinse process ended as a method which adds an oxidizer, the pure water for rinses is poured continuously as it is, it is irradiating ultraviolet rays there, and it excites the oxygen in air, generates ozone, and, in the case of single wafer processing, can also add an oxidizer using the method with which ozone is added with an air current by the pure water for rinses.

[0043] Since the substrate (the thin oxide film is already formed in the silicon front face in fact) which has the silicon front face in which the oxide film was formed does not have a possibility that a water mark may occur, it can be dried by the conventional approaches, such as IPA steam seasoning and spin desiccation.

[0044] after washing by this invention, or etching, and a pure-water rinse -- the washing station for forming an oxide film after a rinse process and enforcing the approach of drying can carry out a means by which the pure water which added the oxidizer is supplied, by adding to the conventional washing station, and can offer in process or the washing station which prevents generating of a water mark with a simple means.

[0045]

[Example]

[Example 1] An example is explained with reference to a drawing. In the process which polycrystal-izes the amorphous silicon formed on the glass substrate by laser crystallization, what used this invention for the process which removes the natural oxidation film formed in the amorphous silicon front face before laser crystallization by wet etching (drawing 1), and the thing (drawing 2) which does not use this invention for a comparison are shown.

[0046] Laser crystallization of the substrate with which 2000A of substrate oxidation silicon film 2 was formed upwards on the glass substrate 1 (#1737 by Corning, Inc. are used in this example), and 300-500A of 400A of amorphous silicon film 3 was formed typically is carried out. Amorphous silicon 3 is formed by the plasma-CVD method or the reduced pressure heat CVD method. Formation of a water mark changes also with formation approaches, and the silicon film formed by the plasma-CVD method tends to generate a water mark rather than the silicon film formed by the reduced pressure heat CVD method. The film formed by the plasma-CVD method when this observed the formed silicon front face has more cluster-like irregularity than the silicon front face formed by the reduced pressure heat CVD method, and this is surmising that it is the cause.

[0047] In this example, since this invention was carried out to the thing in which amorphous silicon was formed, by the plasma-CVD method, it was further effective. In the film of the amorphous silicon formed by the plasma-CVD method, the hydrogen of 5 - 30 atom % is added. In order to heat the amorphous silicon which absorbed the laser beam and to emit hydrogen rapidly if laser crystallization is performed while this hydrogen had been added, many holes like a crater will be made.

[0048] Therefore, a dehydrogenation process is performed in order to extract the hydrogen in amorphous silicon 3 before laser crystallization. In 350-450-degree C nitrogen-gas-atmosphere mind, for 30 - 60 minutes, a grade, it is putting and a dehydrogenation process is a process which decreases the hydrogen in amorphous silicon 3 to about 1 atom % extent about a substrate. Although this dehydrogenation process is performed in nitrogen-gas-atmosphere mind, the natural oxidation film 4 is formed in the front face of the amorphous silicon 3 for the existence of slight oxygen or air (drawing 1 (A), drawing 2 (A)).

[0049] Since this natural oxidation film 4 is not controlled, thickness and its impurity to contain are also

various. Therefore, if laser crystallization is performed with this natural oxidation film 4 left, variation and the crystallization degree of silicon will change [absorption of laser] for every processing with locations by the thickness of the natural oxidation film 4 again. Furthermore, the impurity in the natural oxidation film 4 which the impurity contains will be spread in silicon.

[0050] Removal of this natural oxidation film 4 is needed before a laser crystallization process. As the approach of removal, the spin etcher equipment (EMUSE tech company make) of single wafer processing is used. Etchant and pure water are sprayed on a substrate from a nozzle to the substrate which this equipment is horizontal, makes rotate a substrate, and is rotating, and desiccation is the spin desiccation method which sprays on the substrate turning around nitrogen and it is made to dry, rotating a substrate.

[0051] In about 20 seconds, the natural oxidation film 4 is removed by buffer fluoric acid (in this example, the buffer fluoric acid of the mixing ratio of fluoric acid:ammonium fluoride =1:50 was used.) as etchant for removal of the natural oxidation film 4. Since there is a residual of buffer fluoric acid, in order to flush this, the rinse by pure water is performed in the front face on which amorphous silicon 3 is exposed for 2 minutes. After completing a rinse, a substrate is dried by spin desiccation and it takes out, and with **, like drawing 2 (B), after waterdrop 5 is made in the middle of spin desiccation and it dries, the water mark 6 is made like drawing 2 (C).

[0052] Since absorption of the laser of the part where the water mark 6 exists is high when laser crystallization by excimer laser is performed to amorphous silicon 3 like drawing 2 (D), while this water mark 6 had existed in the front face, both NG polycrystalline-silicon field 8 with many ridges (condition whose front face was considerably ruined), and the polycrystalline-silicon field 7 of a field without the water mark 6 exist in the part of the water mark 6 like drawing 2 (E).

[0053] Even if the water mark 6 sees the substrate after desiccation, in almost all cases, the existence does not understand it. Since it is considered to be a very thin silicic acid, but, when laser crystallization is carried out, it is begun, and the existence understands it. As for the front face of NG polycrystalline silicon field 8, there are many ridges after laser crystallization, and it is almost impossible to form a transistor in the field.

[0054] When this invention is used, the process which removes the natural oxidation film 4 and carries out a rinse with pure water is the same, but after carrying out a rinse for 2 minutes, ******, coincidence, or the pure water for rinses is stopped for the pure water which added ozone after that on amorphous silicon 3 front face from the nozzle which spouts the pure water which added ozone beside the nozzle for rinses. After forming about 10A oxide film 9 in the front face of deed amorphous-for 3 minutes silicon 3, spin desiccation of the rinse by the pure water of ozone addition is carried out.

[0055] As shown in drawing 1 (B), waterdrop 10 is formed during spin desiccation, but as shown in drawing 1 (C), a water mark is not formed after desiccation of waterdrop 10 after spin desiccation. Therefore, when the amorphous silicon 3 by laser crystallization shown in drawing 1 (D) is crystallized by the polycrystalline silicon 11 shown in drawing 1 (E), polycrystalline silicon becomes the homogeneous polycrystal film and its formation of a thin film transistor etc. is easy for 11.

[0056] Or the oxide film formed in the silicon front face by the pure water of ozone addition lengthens rinse time amount by the pure water concerned, it can thicken thickness by increasing the amount of ozone. Although it is also possible to make thickness into 30A or more, that it takes rinse time amount and since an oxidation rate will become quick and it will be easy to generate dispersion between substrates of thickness if the amount of ozone is made to increase, 10-30A is the optimal.

[0057] Specifically, as for an ozone addition, as for rinse time amount, for 2 - 5 minutes is optimum dose in 3-10 ppm. At this example, about 10A of oxide films is formed in [rinse time amount] 3 minutes with the ozone addition of 5 ppm.

[0058] The addition approach of ozone is producing the pure water of ozone addition for the ozone which electrolyzed pure water and was generated using the gas permeable membrane made of a fluororesin. In for 2l./of amount of water, in this example, hydronalium oxy-JIKARU manufacture **** (UOW1A mold) which can generate the 6mg /of the amounts of ozone l. is used with the solid-state polyelectrolyte (SPE) water electrolysis method. Moreover, when not using ozone, even if it adds a hydrogen peroxide 5 to 20%, the same oxide film can be formed. However, when it is with a hydrogen peroxide, since a hydrogen peroxide [activity / front face] remains if it is not made to dry after performing the rinse in pure water again after

oxide-film formation, it becomes an indispensable process.
[0059] [Example 2] The washing station for carrying out this invention to drawing 4 is shown. It has two-room composition of the rinse room 42 which performs even the rinse and desiccation by the pure water with which the oxidizer for forming the oxide film before desiccation by the etching chamber 41, the pure-water rinse, and this invention for etching the natural oxidation film formed in the silicon front face was added.
[0060] In an etching chamber, buffer fluoric acid blows off from a nozzle 44 first, and a substrate 48 rotates the substrate 48 which has a silicon front face by the rolling mechanism 43. Buffer fluoric acid removes the natural oxidation film on breadth and the front face of silicon all over substrate 48 revolving.
[0061] The substrate which etching of the natural oxidation film ended is conveyed at the rinse room 42 so that a substrate front face may not dry. Conveyance is carried out by making the inside where underwater conveyance or pure water is blowing off convey. Pure water is poured on the substrate 49 which pure water blows off from the pure-water nozzle 46, and rotates the substrate 49 conveyed at the rinse room 42. Since the substrate 49 is rotating by the rolling mechanism 44, pure water spreads all over a substrate. While pure water is blowing off from the pure-water nozzle 46, the pure water with which the oxidizer was added blows off from the oxidation nozzle 45 to a substrate 49. The pure water with which the oxidizer was added blows off from the oxidation nozzle 45, and supply of the pure water from the pure-water nozzle 46 stops after 1 - 3 seconds. Oxide-film formation only by the pure water with which the oxidizer was added is performed. Supply of the pure water of oxidizer addition stops after that, and pure water blows off from the pure-water nozzle 46 again.
[0062] After flushing the residual of the pure water of oxidizer addition, the pure-water supply from the pure-water nozzle 46 stops, the rotational frequency of a substrate is raised from the nitrogen nozzle 47 with jet of nitrogen, and spin desiccation of the substrate is carried out.
[0063] The washing station by this invention can respond only by carrying out easy reconstruction for conventional equipment, without newly introducing a facility, since it can constitute only from adding one oxidation nozzle 45 which supplies the pure water which added the oxidizer to the pure-water nozzle 46 for the rinses of the washing station by the conventional technique. Washing of silicon by the washing station of this invention can realize the washing station which can prevent formation of a water mark by forming a thin oxide film in a silicon front face.
[0064]
[Effect of the Invention] This invention is carried out with the gestalt described above, and does so effectiveness which is indicated below.
[0065] Generating of the water mark after desiccation can be prevented by losing silicon among three conditions that form an oxide film in a silicon front face, and a water mark is formed by the simple method of drying a substrate after the pure-water rinse which added the oxidizer for generating of the water mark which will be formed if a substrate is dried at the process of wet washing which makes a silicon front face expose, or wet etching.
[0066] By applying this invention to the laser crystallization process of amorphous silicon, it can crystalize to homogeneous polycrystalline silicon with few ridges, and a water mark does not become trouble in a subsequent thin film transistor production process.

[Translation done.]

* NOTICES *

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing showing the washing process using this invention.
[Drawing 2] Drawing showing the washing process by the conventional technique.
[Drawing 3] Drawing showing the generating principle of a water mark.
[Drawing 4] Drawing showing the washing station using this invention.
[Description of Notations]
1 Substrate
2 Substrate Film
3 Amorphous Silicon
4 Natural Oxidation Film
5 Ten Waterdrop
6 Water Mark
7 11 Polycrystalline silicon
8 NG Polycrystalline Silicon
9 Oxide Film

[Translation done.]

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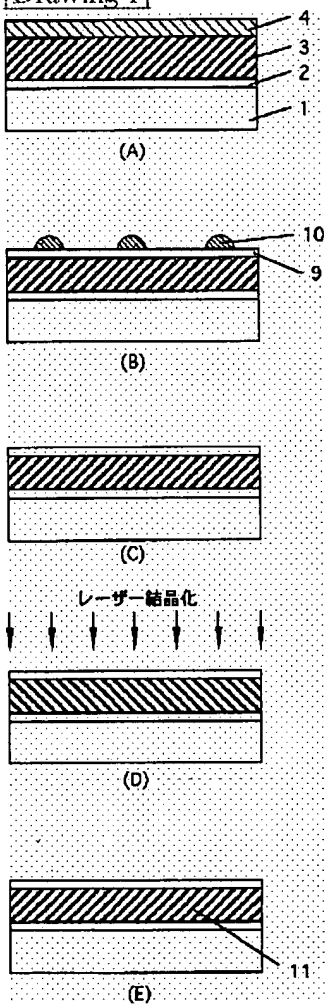
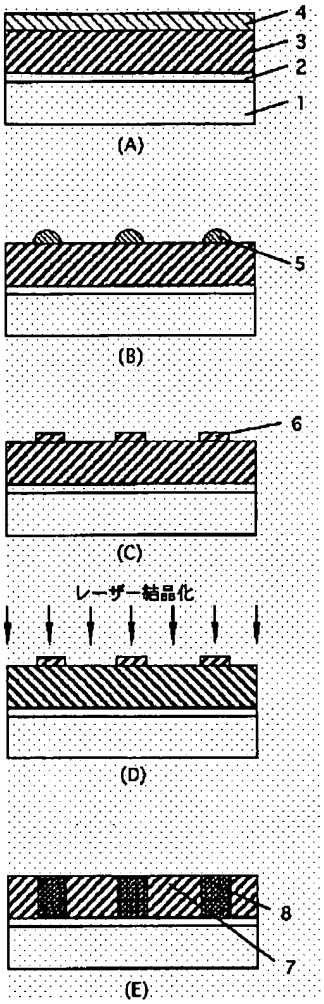
DRAWINGS

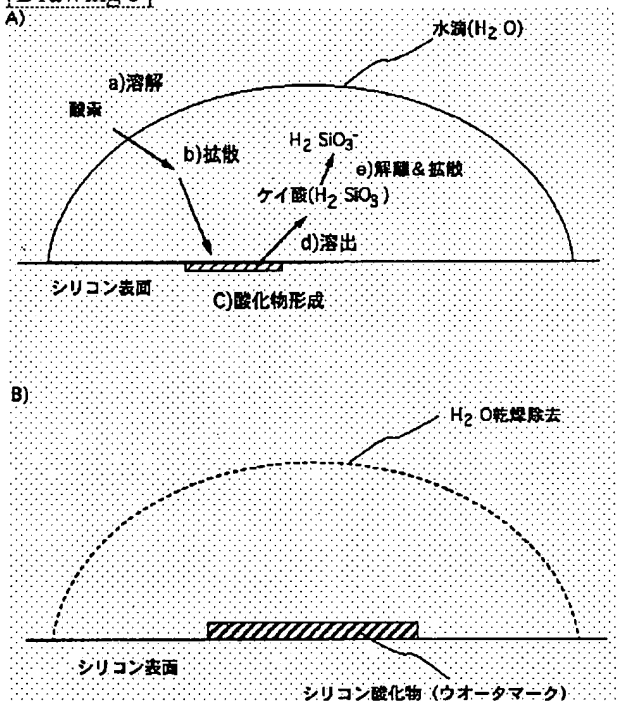
[Drawing 1]



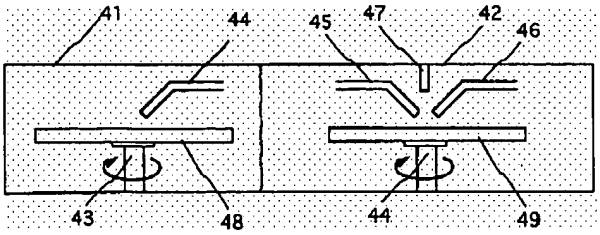
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]